High-spin Cyclopentadienyl Complexes, Part 6. $\sigma/\pi$-Rearrangement of Aryl Ligands Connected to Cyclopentadienyliron Fragments

Mark W. Wallasch, Felix Rudolphi, Gotthelf Wolmershäuser, and Helmut Sitzmann

FB Chemie der TU Kaiserslautern, Erwin-Schrödinger-Str. 54, D-67663 Kaiserslautern, Germany

Reprint requests to Prof. Dr. Helmut Sitzmann. Fax: 0631/205-4399.
E-mail: sitzmann@chemie.uni-kl.de

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Dedicated to Professor Otto J. Scherer on the occasion of his 75$^{\text{th}}$ birthday

Dimeric tri(tert-butyl)cyclopentadienyliron(II) bromide [Cp‴Fe(µ-Br)]$_2$ (1) reacts with phenylmagnesium bromide to give the dinuclear di(cyclohexadienyldiene) complex [(Cp‴Fe)$_2$(µ,η$^5$:η$^5$-H$_5$C$_6$=C$_6$H$_5$)] (2), and with mesitylmagnesium bromide either to the dinuclear complex [Cp‴Fe(µ,η$^1$:η$^5$-C$_6$H$_2$Me$_3$)Fe(Br)Cp‴] (3) or to the mononuclear mesityl complex [Cp‴FeC$_6$H$_2$Me$_3$] (4), depending on the reaction conditions. The mesityl complex 4 undergoes rearrangement and adds via the mesityl ipso carbon atom to bromide 1 with formation of 3. A similar reaction occurs with the nickel analog of bromide 1. In the latter case, however, mesityl is replaced by tolyl during reaction in toluene, with phenyl in benzene, and remains unchanged if the reaction is carried out in pentane solution. An electrophilic attack at the arene solvent used is discussed for the exchange reaction. For the crystallographically characterized complexes 3 and [Cp‴Fe(µ,η$^1$:η$^5$-C$_6$H$_4$Me)Ni(Br)Cp‴] (5) with a meta-tolyl ligand a significant deviation of the Cp‴Fe fragment from a symmetrical position above the six-membered ring ligand raises questions regarding a possible contribution of a cyclohexadienylidene resonance structure.

Key words: Crystal Structure, Dienyliron Complexes, Aryl Complexes, Carbene Complexes, Tri(tert-butyl)cyclopentadienyl